# Measurements of $CO_2/N_2$ from Mt. Barcroft

Geoffrey Toon, Jean-Francois Blavier, and Bhaswar Sen
Jet Propulsion Laboratory, California Institute of Technology

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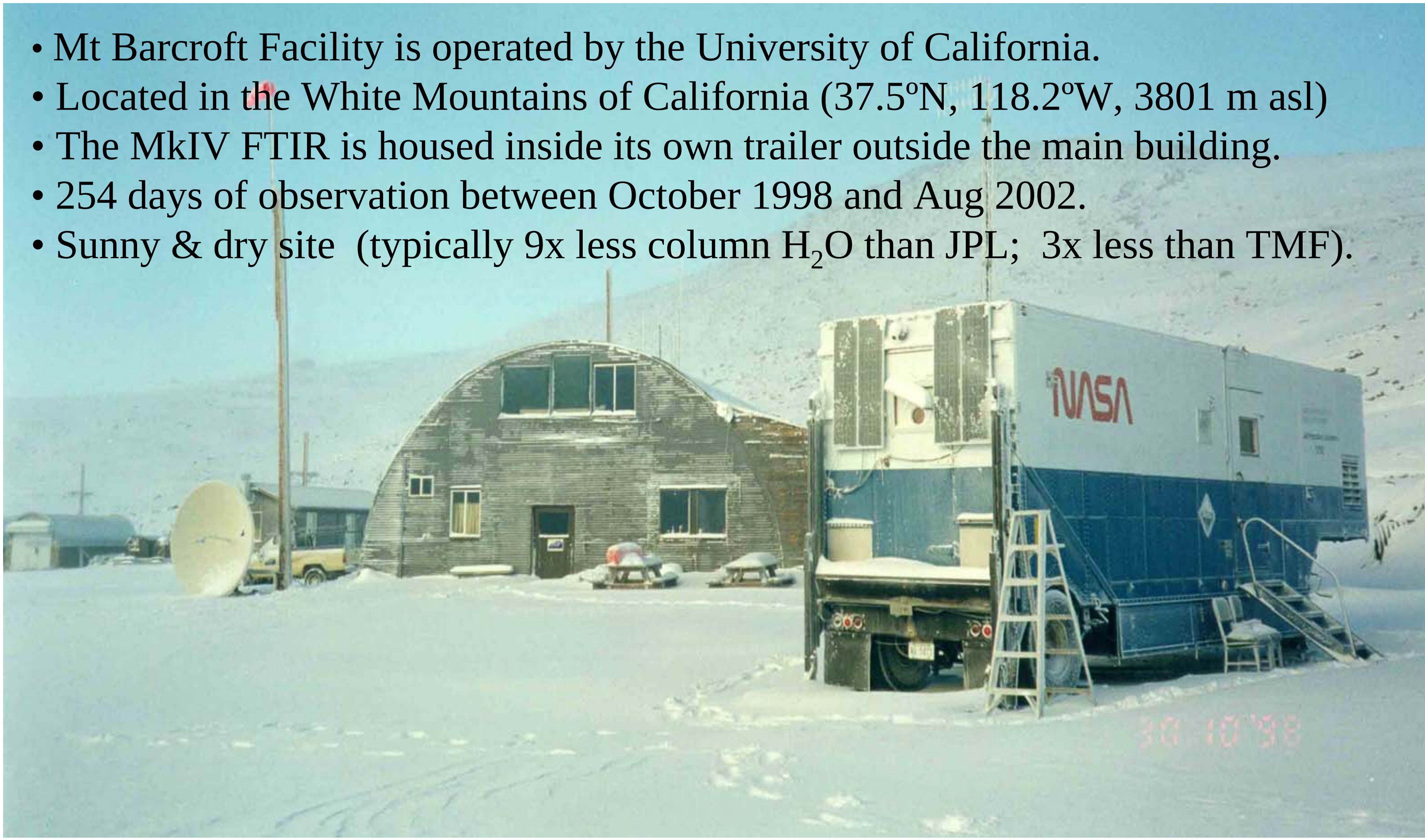
- Mt Barcroft Facility is operated by the University of California.
- Located in the White Mountains of California (37.5ºN, 118.2ºW, 3801 m asl)
- The MkIV FTIR is housed inside its own trailer outside the main building.
- 254 days of observation between October 1998 and Aug 2002.
- Sunny & dry site  (typically 9x less column $H_2O$ than JPL;  3x less than TMF).



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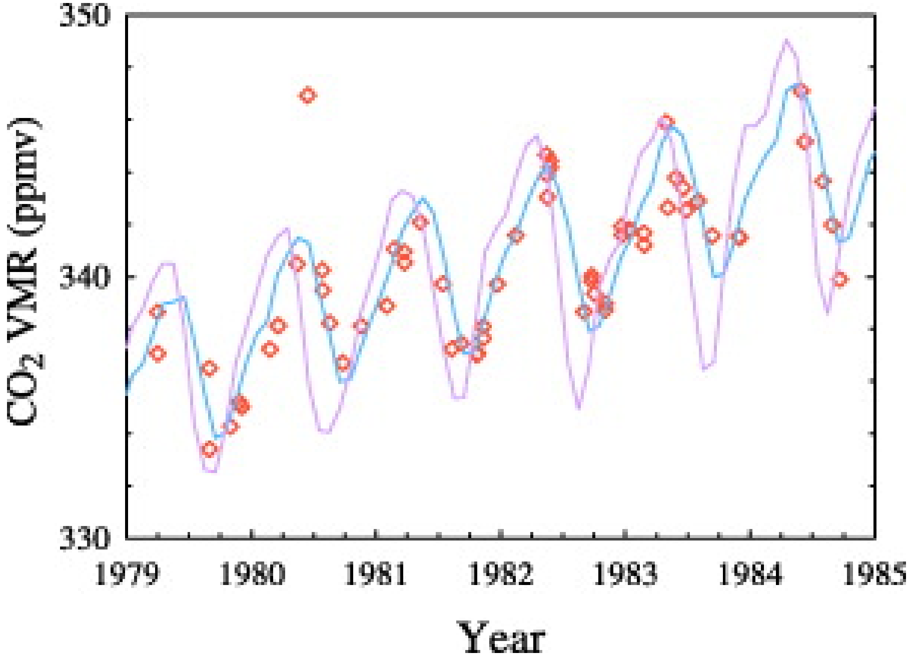
- Atmospheric $CO_2$ has a long lifetime, therefore the impacts of sinks on its atmospheric abundance are very subtle (typically < 1%).
- For atmospheric $CO_2$ measurements to be useful in understanding the carbon cycle, they must therefore be very accurate.

Yang et al. [2002] used Kitt Peak FTIR spectra to show that in the near-IR, $CO_2$ could be measured to ~0.5% precision by use of the $CO_2/O_2$ ratio (right).

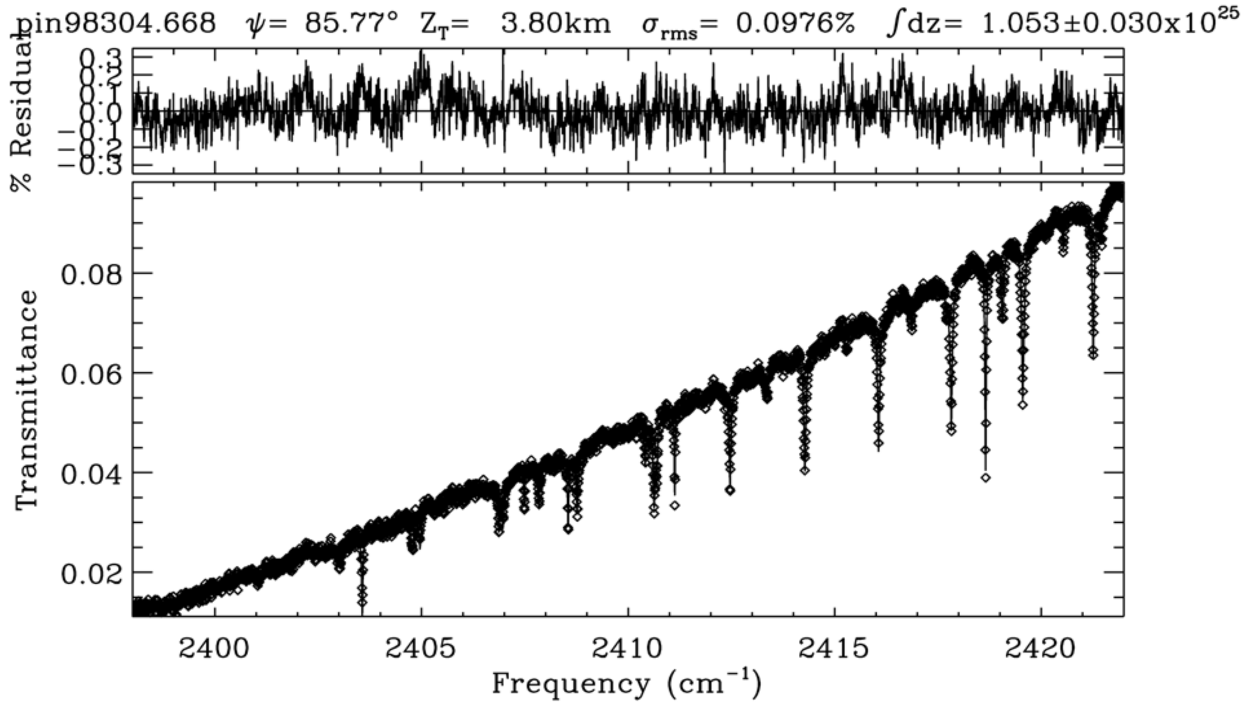
But most of the existing NDSC instruments operate in the mid-IR, where there are no suitable $O_2$ lines.




To assess the precision that $CO_2$ can be measured in the mid-IR, we have analyzed ground-based spectra measured by the JPL MkIV interferometer.

# Measurements of $CO_2/N_2$ from Mt. Barcroft

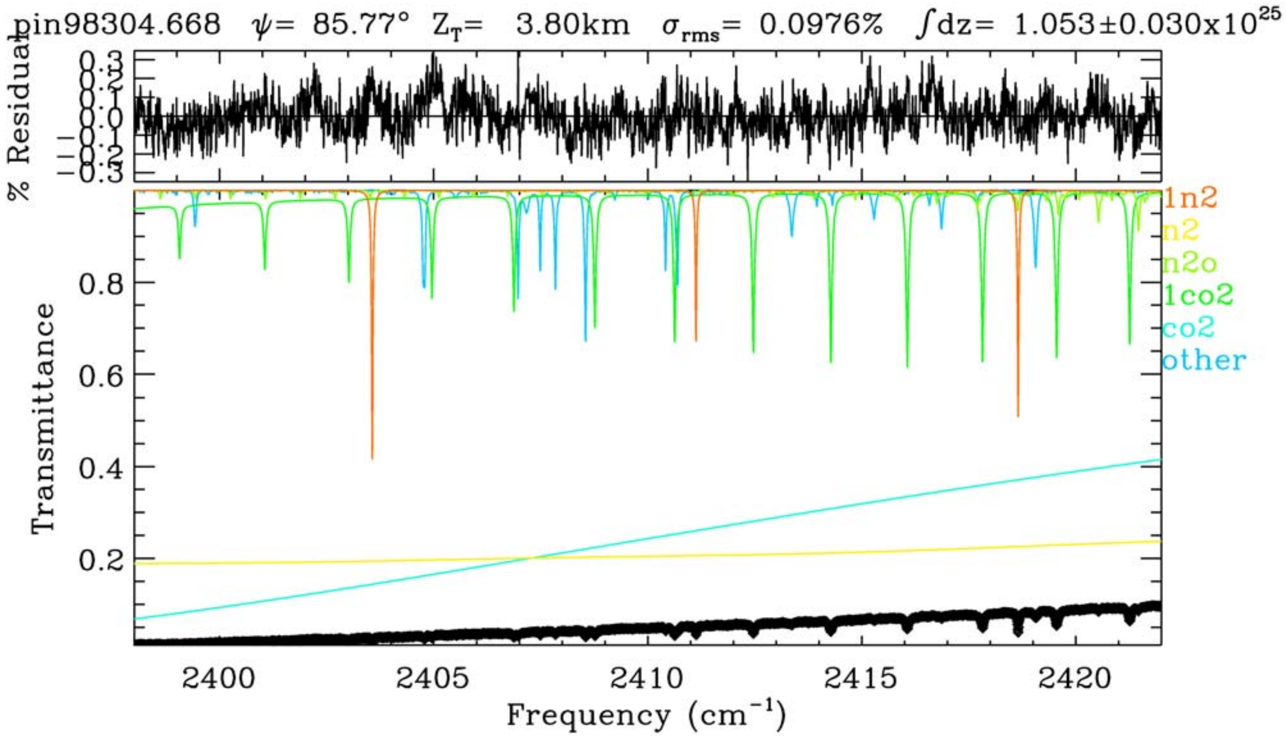
- To accurately retrieve the tropospheric $CO_2$ vmr, it is helpful to simultaneously retrieve a reference gas with an accurately-known vmr profile (i.e. $N_2$). Many systematic errors that are common to $CO_2$ and $N_2$ (e.g. surface pressure, zenith angle, ILS, zero offsets, etc.) will partially cancel in the $CO_2/N_2$ ratio.
- MkIV instrument has access to the $N_2$ quadrupole lines ~2400 $cm^{-1}$ (no NDSC filters).
- Barcroft site has an average pressure of 0.65 atm. Since the predominant absorptions in the 2400 $cm^{-1}$ region vary as $P^2$, $N_2$ can be accurately measured up to 86º zenith angle.



# Measurements of $CO_2/N_2$ from Mt. Barcroft

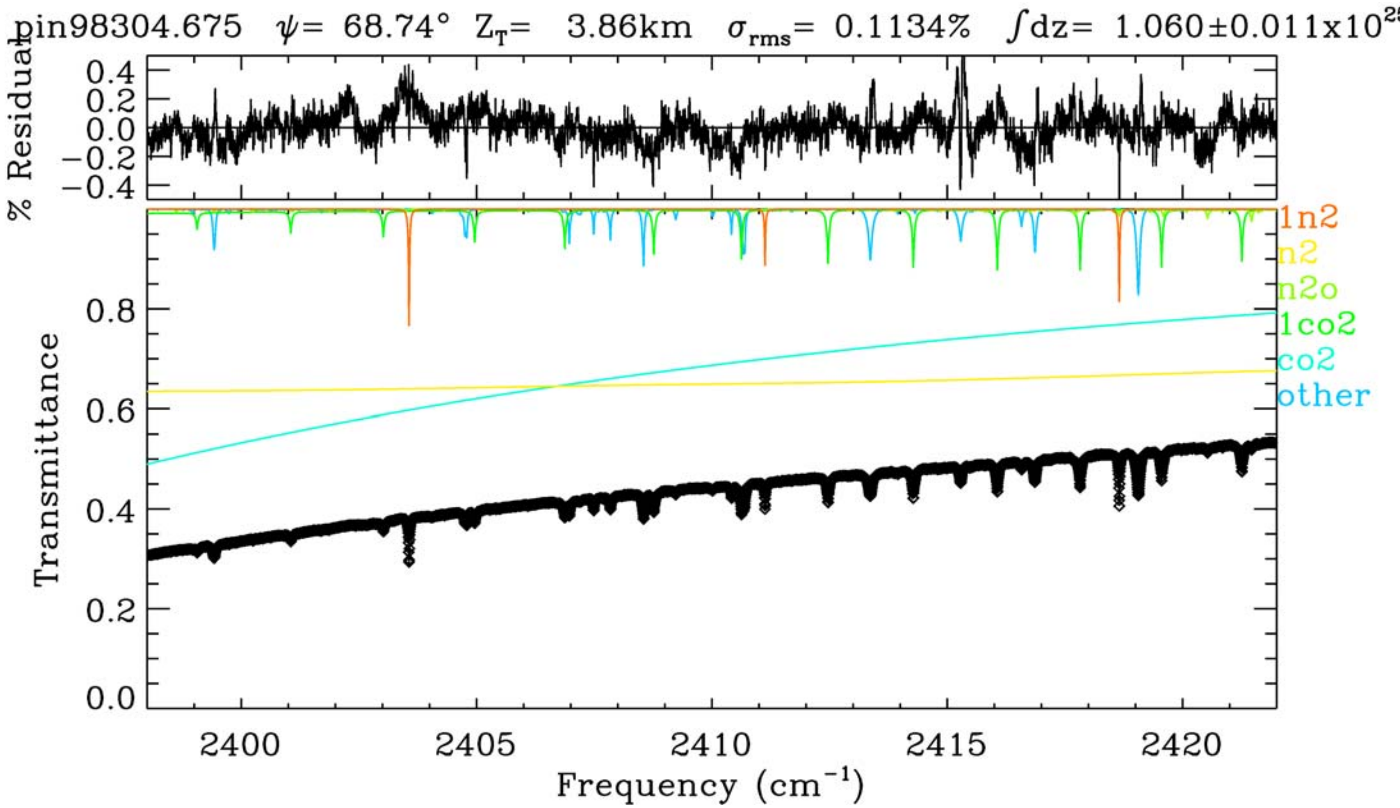
2400 $cm^{-1}$ region also contain absorption from $CO_2$, $N_2O$ , $H_2O$ (weak) and solar features. Continuum absorptions also arise from the $N_2$ CIA and the far-wings of the $\nu_3$ $CO_2$ lines.

$N_2$ can be retrieved to ~3% at 85.77º zenith angle from MkIV Barcroft Spectra.



# Measurements of $CO_2/N_2$ from Mt. Barcroft

- At lower zenith angles, the continuum absorption diminishes, but solar features become more important
- $N_2$ precision improves to ~ 1%

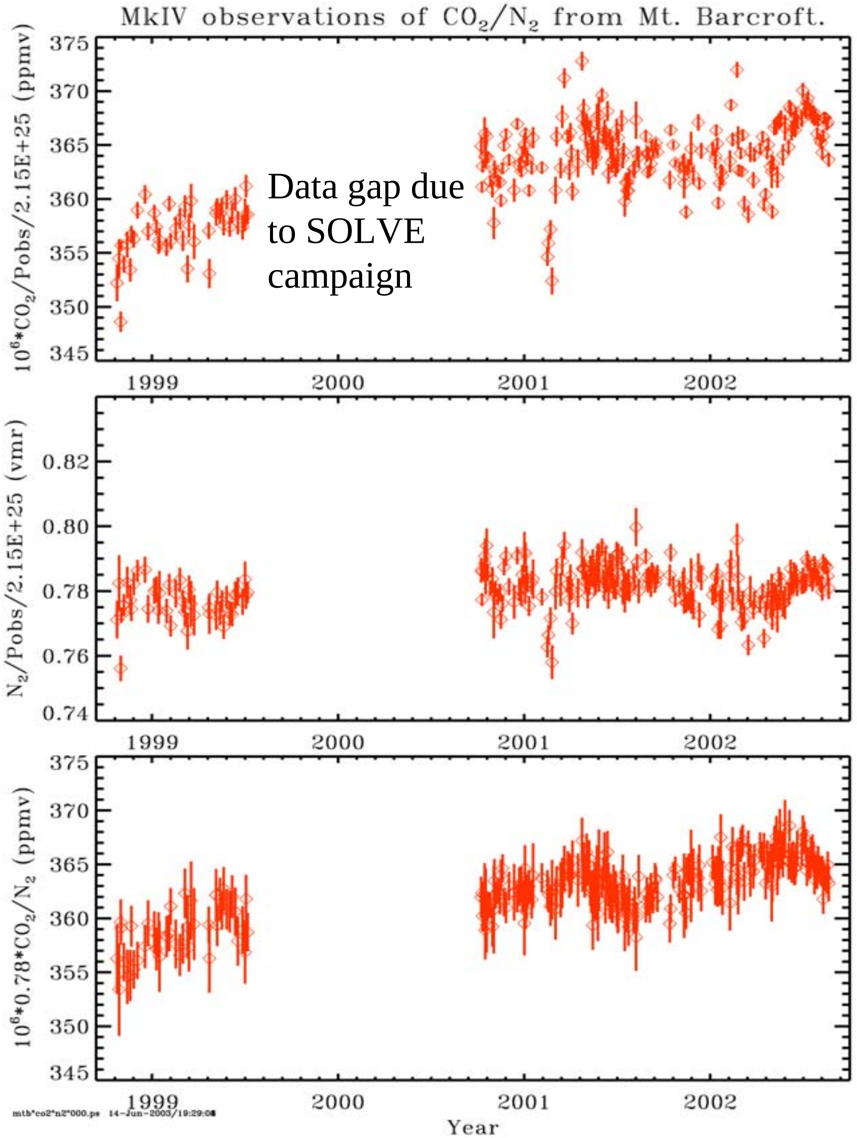


# MkIV measurements of $CO_2/N_2$ from Barcroft

Upper panel shows the daily average retrieved $CO_2$ column amounts divided by surface pressure (Pobs), and 2.15E+25 to express them as ppmv.

Middle panel shows the retrieved $N_2$ column amounts, divided by Pobs and by 2.15E+25. Departures from 0.78 are due to errors (Pobs, pointing, ILS, temperature, zero-level offset, etc.)

Lower panel shows $0.78*CO_2/N_2$. Although the error bars are larger than those of $CO_2$(due to the $N_2$), the scatter is reduced, due to cancellation of systematic error terms.



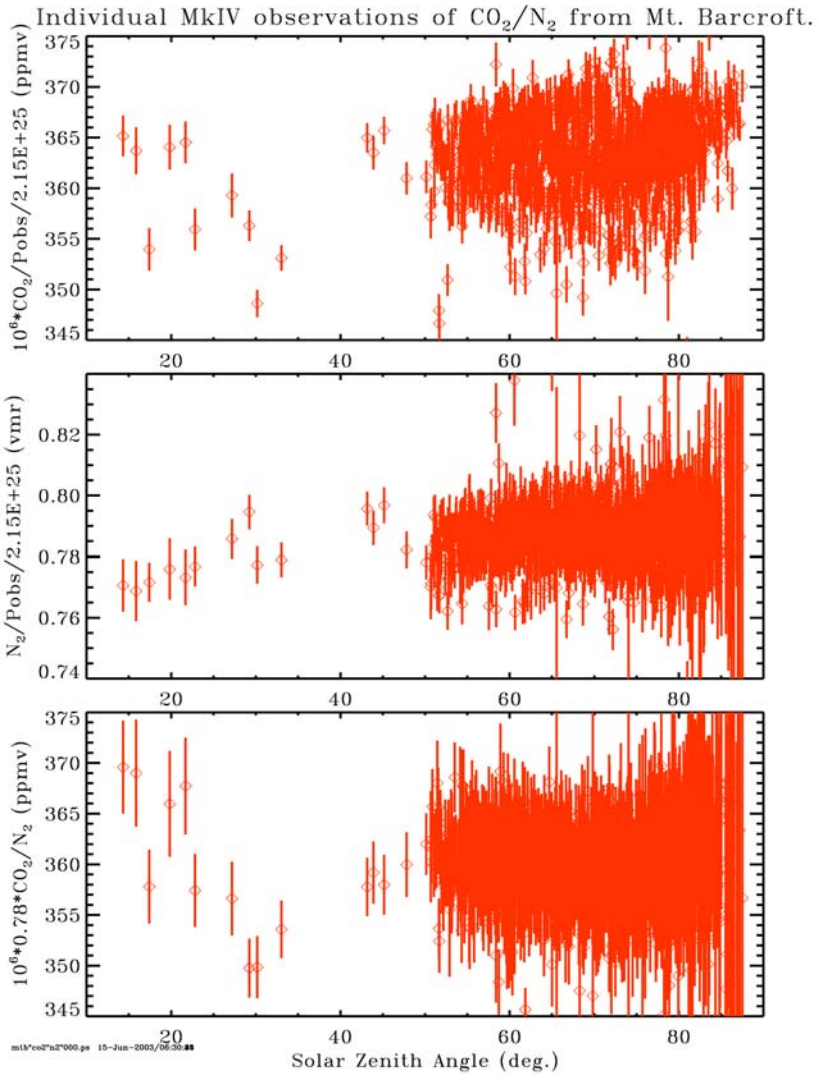
# Airmass-dependence of individual $CO_2$, $N_2$ observations

Examining the airmass dependence of the retrieved $CO_2$ and $N_2$ tests for the presence of systematic errors

$CO_2$ error bars are virtually independent of airmass, due to the use of a large range of $CO_2$ line strengths

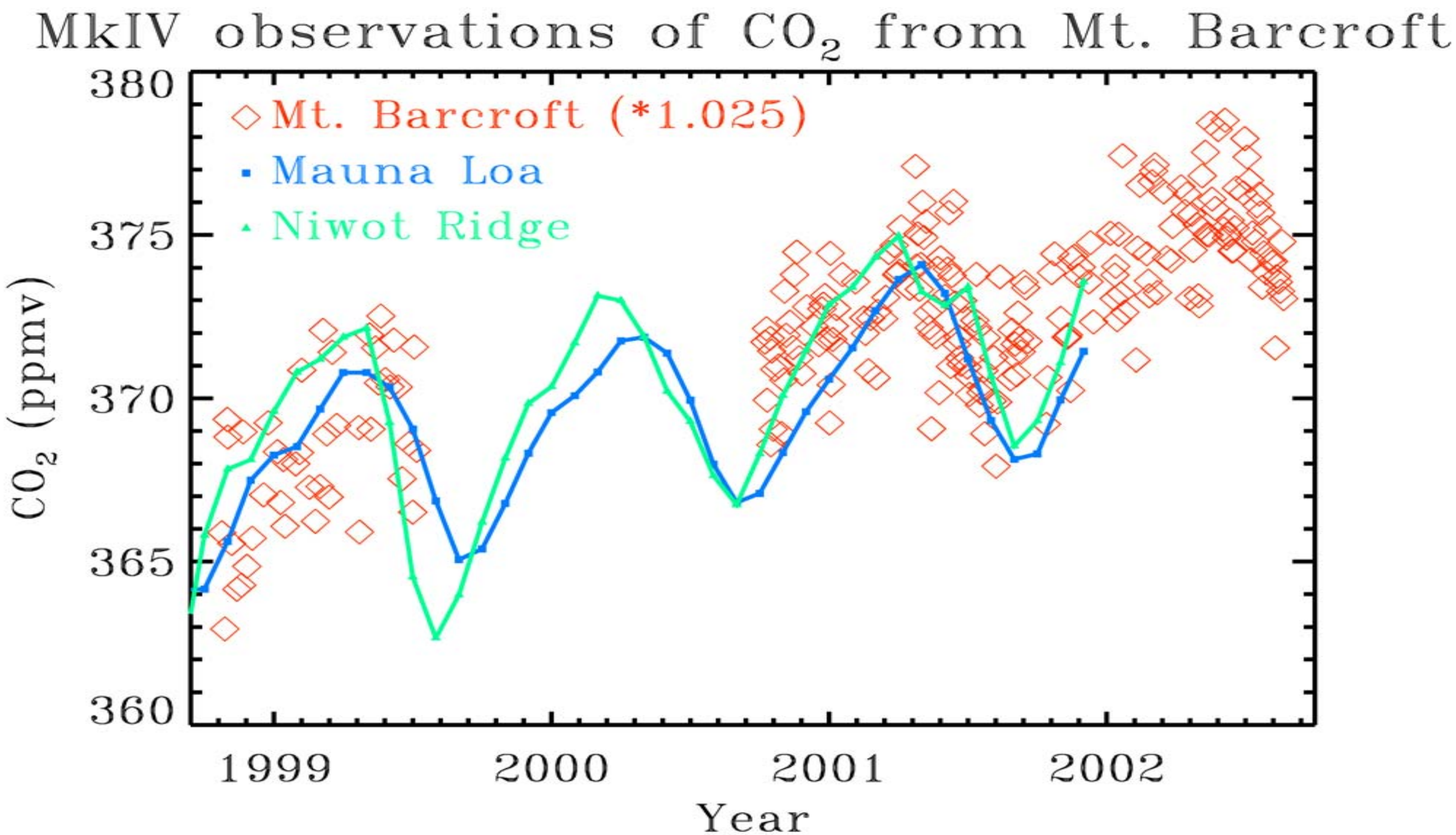
$N_2$ error bars increase rapidly for SZA>85 deg due to 2400 $cm^{-1}$ region becoming blacked out by continuum absorption.

No discernable systematic airmass-dependence (good).



# Daily mean $CO_2$ observations from Mt. Barcroft

- MkIV data was scaled by 1.025 to better match in situ data (spectroscopic error ?)
- Barcroft data show seasonal cycle that is in phase with surface in situ observations from Mauna Loa and Niwot Ridge, but smaller in amplitude (~1%).



# MkIV $CO_2/N_2$ observations - Conclusions

Mid-IR MkIV spectra have demonstrated a $CO_2$ precision ~2 ppm (~0.5%) and probably better since some of the remaining $CO_2$ variability is undoubtedly real.

Agreement with in situ data is poorer than NIR measurements of Yang et al. [2002].

The remote MkIV $CO_2$ observations sample much higher in the atmosphere than surface in situ measurements (due to their column-averaging nature, and due to the fact that Mt Barcroft is higher than Mauna Loa or Niwot Ridge). This may help explain why the MkIV seasonal cycle is smaller than those seen at the surface.

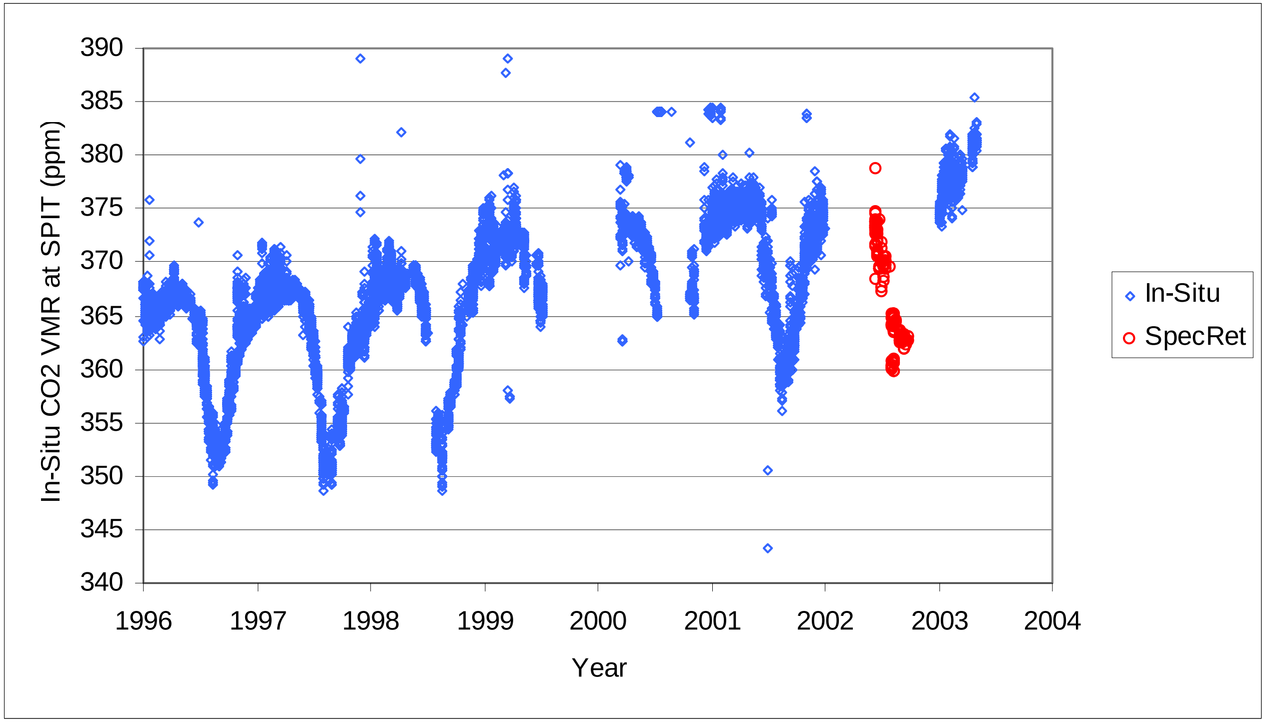
Ratioing by $N_2$ helps cancel systematic errors, improving accuracy, but degrades precision by adding noise from the $N_2$ retrievals (only 3 suitable $N_2$ lines).

To improve precision of $CO_2$ retrievals requires either:

- ratioing by a reference gas with more absorption lines, e.g. $O_2$ in the NIR
- exceptional control over instrumental systematic errors allowing direct use of $CO_2$ columns without ratioing.

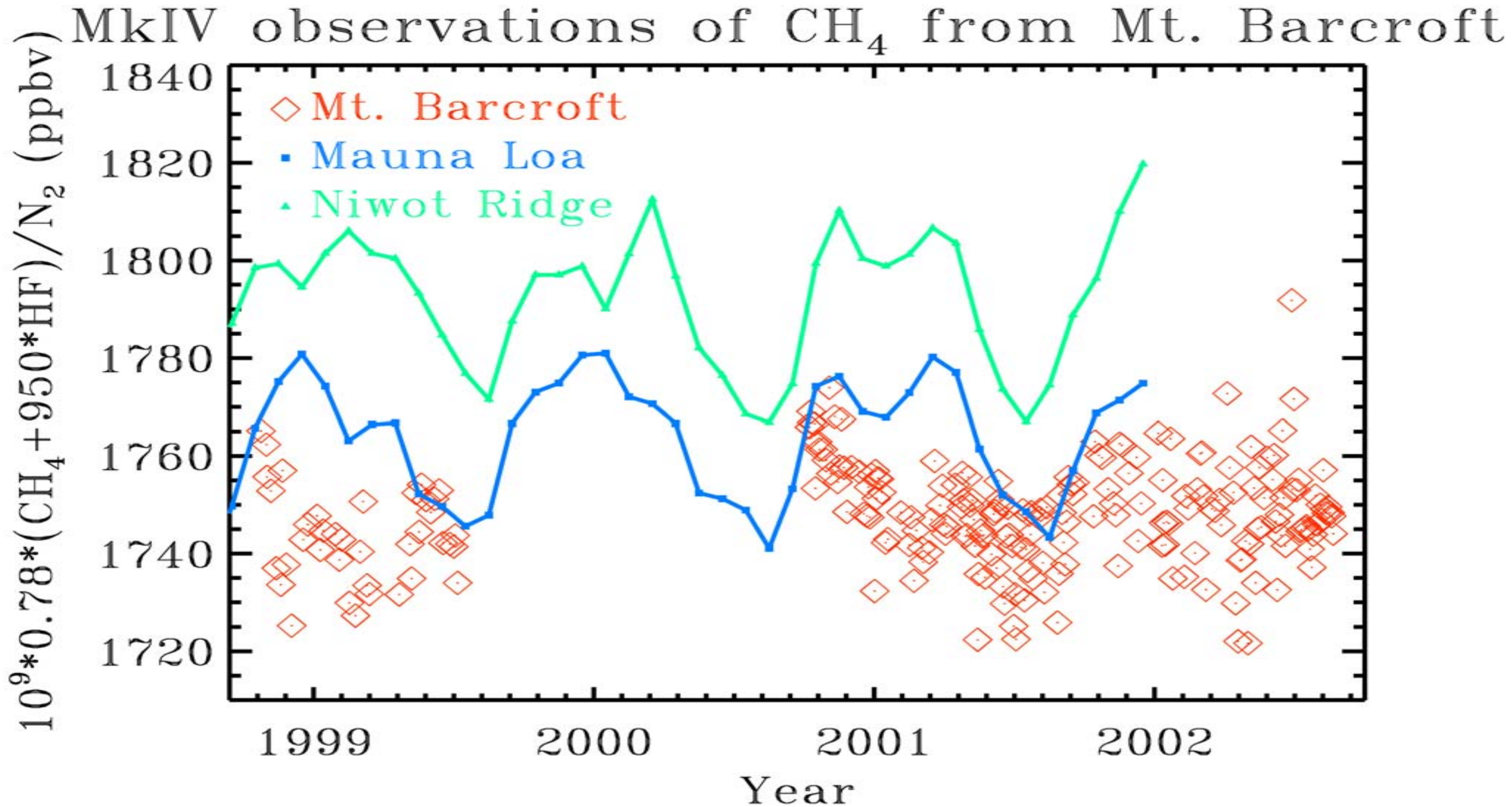
# NIR $CO_2$ observations from Spitsbergen

Analyzed by Zhonghua Yang using spectra provided by Justus Notholt
Used the 6220 $cm^{-1}$ $CO_2$ band and the 7900 $cm^{-1}$ $O_2$ band
Seasonal variation of $CO_2$ at 79ºN is ~5%, much larger than mid-latitudes.



# Daily mean $CH_4$ observations from Mt. Barcroft

Used same spectra as for $CO_2$
Followed same procedure as Washenfelder et al. to correct for stratospheric $CH_4$ variations due to changes in tropopause altitude.



# $N_2$, $CO_2$ and $CH_4$ windows used in analyses

| Window | Mean_Col | Std_Err | $\chi^2/N$ |
|---|---|---|---|
| co2_2482 | 1.0126 | 0.0009 | 0.8549 |
| co2_2486 | 0.9725 | 0.0008 | 1.2176 |
| co2_2626 | 1.0177 | 0.0003 | 0.7190 |
| co2_3161 | 0.9877 | 0.0006 | 0.5473 |
| co2_3204 | 0.9871 | 0.0003 | 0.5819 |
| co2_3315 | 0.9963 | 0.0003 | 0.5906 |
| co2_4879 | 1.0263 | 0.0010 | 0.5592 |
| co2_4883 | 0.9783 | 0.0009 | 0.6220 |
| co2_4885 | 0.9610 | 0.0006 | 0.4393 |
| co2_4886 | 1.0118 | 0.0007 | 0.4210 |
| co2_4887 | 1.0009 | 0.0007 | 0.2884 |
| co2_4888 | 0.9992 | 0.0008 | 0.3898 |
| co2_4890 | 0.9940 | 0.0008 | 0.3492 |
| co2_4891 | 0.9809 | 0.0006 | 0.3705 |
| co2_4892 | 0.9956 | 0.0007 | 0.3979 |
| co2_4902 | 0.9862 | 0.0006 | 0.4354 |
| co2_4912 | 1.0104 | 0.0009 | 0.2384 |
| co2_4919 | 1.0493 | 0.0007 | 0.3148 |
| co2_4922 | 1.0292 | 0.0006 | 0.3586 |

| Window | Mean_Col | Std_Err | $\chi^2/N$ |
|---|---|---|---|
| n2_2403 | 0.9765 | 0.0004 | 0.5600 |
| n2_2411 | 1.0012 | 0.0006 | 0.6853 |
| n2_2418 | 1.0232 | 0.0004 | 0.5025 |

| Window | Mean_Col | Std_Err | $\chi^2/N$ |
|---|---|---|---|
| ch4_2599 | 0.9841 | 0.0003 | 0.3495 |
| ch4_2602 | 0.9973 | 0.0003 | 0.6069 |
| ch4_2903 | 0.9859 | 0.0002 | 0.4860 |
| ch4_4268 | 0.9889 | 0.0004 | 0.5386 |
| ch4_4277 | 0.9956 | 0.0003 | 0.4543 |
| ch4_4361 | 1.0552 | 0.0004 | 0.3139 |
| ch4_4376 | 1.0069 | 0.0003 | 0.3222 |
| ch4_4385 | 1.0009 | 0.0003 | 0.3675 |
| ch4_4420 | 0.9957 | 0.0006 | 0.2515 |
| ch4_4424 | 1.0046 | 0.0005 | 0.3666 |
| ch4_4469 | 0.9945 | 0.0003 | 0.6660 |
| ch4_4470 | 0.9922 | 0.0005 | 0.4408 |
| ch4_4471 | 0.9904 | 0.0007 | 0.3599 |
| ch4_4489 | 1.0031 | 0.0003 | 0.3071 |
| ch4_4500 | 1.0172 | 0.0003 | 0.4026 |
| ch4_4511 | 1.0137 | 0.0004 | 0.2823 |
| ch4_4522 | 1.0207 | 0.0003 | 0.5124 |
| ch4_4567 | 0.9769 | 0.0003 | 0.4903 |
| ch4_4578 | 1.0116 | 0.0006 | 0.2217 |
| ch4_4602 | 0.9889 | 0.0006 | 0.5023 |